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THE DEVELOPMENT OF A METHOD TO MEASURE NO_x EMISSIONS FROM SOILS

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ABSTRACT

An automated chamber technique for measuring NO_x emissions from soils was developed and operated in the field at Egbert, Ontario, towards the end of the 1988 Canadian Atmospheric Chemistry Study. Field NO_x emissions were found to be in the range of 0.91 to 2.7 ng(N) $m^{-2}s^{-1}$. These rates are comparable to values reported in the literature. It is recommended that additional studies be carried out to determine natural NO_x emissions in Southern Ontario to establish reliable input data for regional oxidant models.

1.0 INTRODUCTION

1.1 Background

This report describes a chamber apparatus constructed to measure natural nitrogen oxide (NO and NO_2) emissions from soils and documents preliminary measurements made as part of the 1988 field campaign of the Canadian Atmospheric Chemistry Study.

The interest in defining NO_x (NO and NO_2) sources to the atmosphere arises because NO_x participates in a complicated series of chemical reactions with various volatile organic compounds (VOC's) to give rise to photo-chemical oxidants such as ozone (O_3) and PAN (peroxyacetylnitrate) which have been implicated in health effects and crop damage. Well

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known sources of NO_x are motor vehicles and the combustion of fossil fuels for heating and electricity generation. VOC's arise mainly from chemical industries and motor vehicles. Less well known is the fact that significant natural emissions of VOC's and NO_x also occur. Natural hydrocarbons, such as isoprene and terpene, are emitted by vegetation and NO_x is released from soils through microbial action. About 15% of the tropospheric source term for NO_x is estimated to originate from soil, whereas about 63% is anthropogenic due to fossil fuel combustion and biomass burning (Mackay, 1988).

A natural oxidant background therefore exists in the atmosphere. Oxidant levels are expected to be increased by the addition of anthropogenic pollutants, however, the relation between the amount of a pollutant released at a particular point and the oxidant levels resulting far downwind is very complicated. The impact of a source, or set of NO_x sources, on oxidant levels must be determined by calculation using mathematical models which describe oxidant formation, transport and depletion on a regional basis. A knowledge of the natural emissions of key reactants is important to model correctly the impact of NO_x emissions from industrial activity, particularly as natural emissions occur over large regional scales and form the "chemical background" into which anthropogenic pollutants are emitted.

The present work was therefore initiated to develop the methods by which to help form an information base on natural NO_x emissions for Southern Ontario. The long-term goal of this work is to define natural NO_x sources on a regional and seasonal basis for Southern Ontario as an input to modelling studies.

The NO_x flux measurement procedure used was based on the closed chamber technique employed by various groups in Europe and the USA (Johansson 1984, Johansson and Granat 1984, Parrish et al 1987, Williams et al 1987, Anderson and Levine 1987). Field trials using the technique were undertaken within the Canadian Atmospheric Chemistry Study which was part of the larger scale Eulerian Model Field Evaluation Study (EMEFS). Before describing in detail the NO_x emission flux measurement technique and the field results, we briefly describe the scope of the Canadian Atmospheric Chemistry Study and Ontario Hydro's contribution to this study.

1.2 The Canadian Atmospheric Chemistry Study

The Canadian Atmospheric Chemistry Study, which is being carried out under the auspices of the Canadian Institute for Research in Atmospheric Chemistry(CIRAC), of which Ontario Hydro is a member, has two objectives:

- to generate field data to test the predictive capability of the Canadian and US Eulerian long-range transport models (ADOM and RADM), and,

- to advance our understanding of atmospheric chemistry, particularly the role of NO_x vs volatile organic compounds and natural vs anthropogenic emissions in controlling photochemical oxidant concentrations in Ontario.

Ontario Hydro has a stake in the Study because of its emissions of NO_x and the possibility that these may contribute to regional pollutant episodes of the type observed frequently in the summer of 1988 (when the newly introduced Provincial Air Quality Index approached

unacceptable levels, largely as a result of the high ozone concentrations). Ontario Hydro's participation in the Study involved

- the measurement of NO_x emissions from soils,
- the analysis of air samples for volatile organic compounds, and
- the analysis of atmospheric aerosol for particle size and trace elements.

The first of these activities provides information on the importance of natural sources of NO_x, as discussed previously. The second yields information on the levels of natural and anthropogenic volatile organic compounds which, together with NO_x, react to produce ozone and other photochemical oxidants. The last activity provides a means of identifying the sources of polluted air masses. Various emission sources can often be identified by their characteristic trace element signatures.

This report deals only with the measurement of NO_x emissions from soils. Background information on soil NO_x emissions, the factors controlling the emission rate, the atmospheric chemistry of NO_x, etc may be found in an earlier report (Mackay 1988).

2.0 EXPERIMENTAL

2.1 Exposure Chamber

Closed chambers have been used by various investigators to determine gaseous emission fluxes from soils; Johansson and Granat 1984, Parrish et al 1987, Williams et al 1987, Anderson and Levine 1987 have all applied this technique to the nitrogen oxides. In this technique the chamber is placed over a known area of soil and the flux of the gas of interest from the soil to the chamber atmosphere is inferred from the rate of increase of concentration within the chamber (in the case of a sealed chamber), or from the steady state concentration achieved in the chamber (in the case where the chamber is flushed by a steady flow of ambient air or "zero" air). The latter method was chosen as the air flow through the chamber facilitates gas concentration measurements and lessens the perturbation of soil conditions due to the presence of the chamber.

The apparatus is shown schematically in figure 1. The chamber (30 cm x 30 cm x 30 cm) was constructed of polycarbonate sheet and lined internally with Teflon. The air within the chamber was mixed by a fan to ensure a homogeneous atmosphere. In operation, ambient air was drawn through two charcoal traps (to remove NO_x, O_3, etc), dried, and pumped into the chamber at a rate of about 5 L min^{-1}. The chamber was vented directly to the atmosphere. Part of the vent flow was drawn off to measure NO and NO_2 levels in the air exiting the chamber by means of a Luminox LMA-3 NO_2 analyzer with LNC-3 NO converter. A by-pass was provided to analyze the incoming, scrubbed air.

The chamber was mounted on a steel, teflon-lined skirt which was driven into the soil. The joint between the chamber and the skirt can be made fully air-tight by means of a water seal, though this was not used in the field measurements described later. The chamber was designed for automated operation, ie, the chamber could be raised and lowered automatically on a predetermined schedule, and the sample gas stream could be alternated between the bypass

stream and the stream from the chamber (Figure 1). This was done to allow unattended flux measurement (eg, on a half-hourly or hourly basis through a 24h cycle to observe diurnal trends).

Details of the materials used, the testing protocol followed and the automatic operation of the chamber may be found in Appendix A.

2.2 Analysis

The NO_x emission flux may be derived from the chamber measurement as follows. Consider the idealized schematic shown in Figure 2 where air, containing an initial concentration N_{in} of trace gas, is flowed into a chamber of volume V at rate Q. Within the chamber, the gas is emitted by the soil area A at a flux J. If none of the gas is lost by absorption on the chamber walls or by chemical reaction, and the chamber is well mixed (ie, concentrations of the trace gas in the chamber air are uniform), then mass balance requires that the following relationship holds for the difference between the concentrations in the inlet and outlet air streams at time t after the chamber is lowered to the soil.

$$\Delta N = N_{out} - N_{in} = \frac{AJ}{Q} [1 - e^{-tQ/V}] \qquad (1)$$

At large times ($t >> V/Q$), ΔN approaches a steady state value, ΔN_{ss}, equal to AJ/Q. As A and Q are known, the emission flux can be determined from a measurement of ΔN_{ss}. In the experiments described here, charcoal traps were used on the inlet airstream to reduce the inlet concentration, N_{in}, to as small a value as possible, so that $N_{out} \approx \Delta N$.

2.3 Field Tests

The test site was at the Centre for Atmospheric Research Experiments (CARE), Egbert, Ontario operated by the Atmospheric Environment Service of Environment Canada. Vegetation cover was approximately 40% alfalfa and 60% grasses (species undetermined), about 30 cm in height on average.The soil was a fine sandy loam. Details of soil conditions are given in Appendix F.

Surface vegetation was removed by cutting with a sharp blade (being careful not to uproot) until less than 1 cm remained above ground. The steel skirts were hammered into the ground. When the ground was too hard, a shovel was used to break the earth. The skirts were left in place for at least 24 h before data collection began. The apparatus was assembled according to Figure 1. The automated system, while fully operational, was never actually utilized during a normal acquisition run due to time constraints. The data were read directly from the instruments themselves.

3.0 RESULTS

3.1 Characterization of the Chamber Technique

Chamber measurements of emission fluxes are only meaningful if absorption of the emitted gas on the walls of the apparatus is negligible and the presence of the chamber does not significantly perturb the factors that control emission flux. To examine the first point, a number of tests were carried out in the laboratory and in the field. In these tests, the effect of

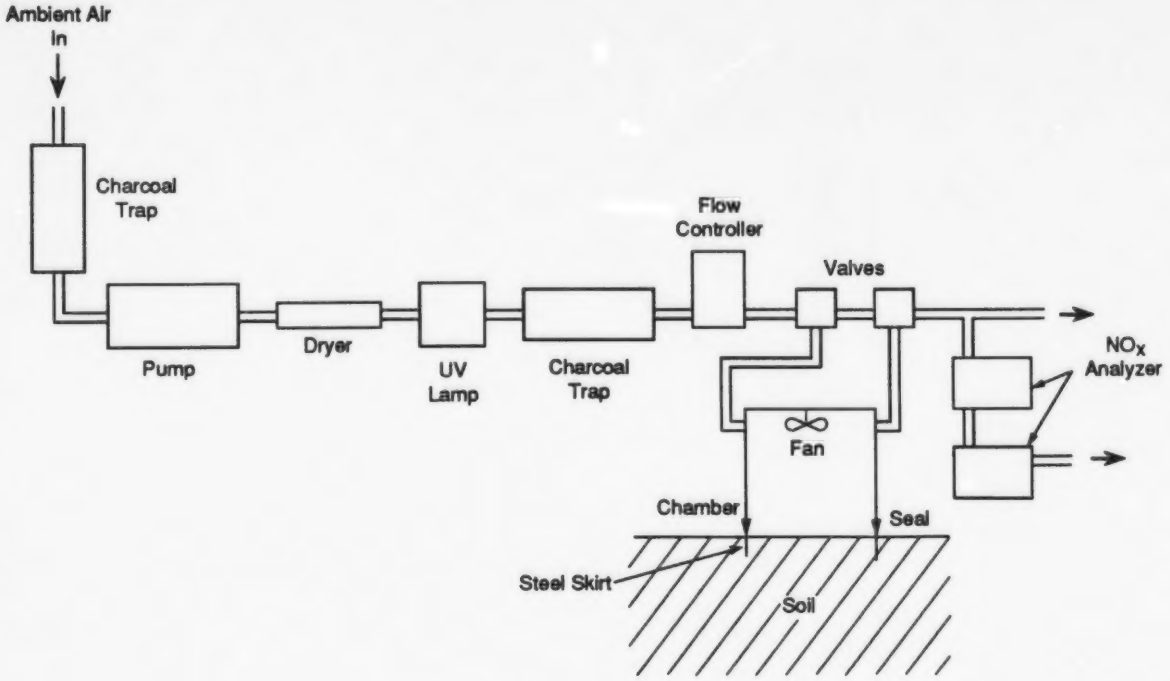

FIGURE 1

SCHEMATIC DIAGRAM OF THE CHAMBER APPARATUS

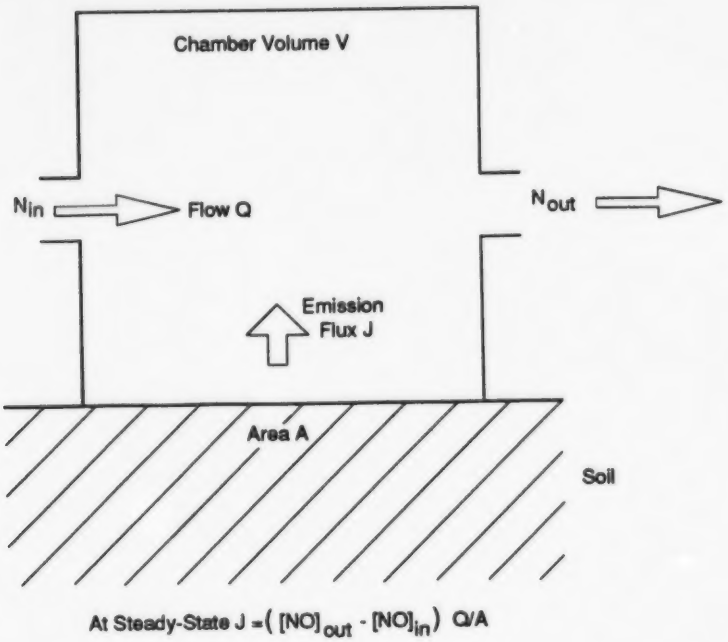

FIGURE 2

SCHEMATIC SHOWING RELATIONSHIP USED TO DETERMINE EMISSION FLUX FROM CHAMBER MEASUREMENTS

operating conditions on chamber pressure, temperature and relative humidity, was examined. As well, the ability of the flow system (ie, chamber-sampling lines, NO converter and NO_2 analyzer) to transfer low concentrations of NO without losses or other disturbances was investigated. The results are discussed in Appendix C.

The size of the chamber vent and the flushing rate affect the pressure in the chamber. (The chamber pressure should be as close to atmospheric pressure as possible so that the natural degassing rate of NO from soil is not affected). This effect was minimized to 0.075 mbars (ie, the chamber pressure was 0.0075% above atmospheric pressure) by proper selection of vent size and flushing rate.

Chamber temperature and relative humidity were both found to be slightly elevated relative to ambient conditions, (by about 1.5-6°C and 2-18% RH after 1 h, depending on ambient conditions). The effect of these differences on measured emission rates is not considered serious relative to other shortcomings of the technique (eg, due to spatial variability of emission rate).

The tests carried out to determine the effect of the various components of the apparatus on the measured concentrations of NO and NO_2 indicated that great care must be exercised to ensure that

- the NO_x analyzer is calibrated regularly, with standards in the low ppb range,
- the tubing is not exposed to high concentrations of NO or NO_2 to avoid contamination through adsorption and degassing, and
- the scrubber used to generate a supply of "zero air" from ambient air is effective.

During the field study, the LMA-3 analyzer was calibrated using a calibrator supplied by Atmospheric Environment Service, new tubing was used and the quality of the "zero air" was monitored. However, additional work should be devoted to optimize these aspects of the technique.

3.2 NO, Emissions from Soils

The soil emissions data consisted of measurements taken over the same 30 cm x 30 cm plot at various times over three days (Tables D1-D4 of Appendix D). Measurements were also made over a second plot approximately 2 m away (Table D5 of Appendix D). Although the quantity of data collected was limited, some useful information was obtained. The NO_2 values were generally very low (less than 10% of the NO) suggesting that little NO_2 was released, or that NO_2 was absorbed or converted by the apparatus. This should be investigated further by introducing an air stream containing a known concentration of NO_2 into the chamber.

Figure 3 shows an example run, where the NO concentration in the chamber is plotted against time. It can be seen that the chamber concentration rises to a steady state value of approximately 4.8 ppbv after about 10 to 20 minutes. Also shown is a theoretical curve based on equation (1) with an assumed steady state value of 4.8 ppbv and time constant for exchange in the chamber of $\tau = V/Q = 5.1$ min. The experimental results agree reasonably well with the theoretical curve.

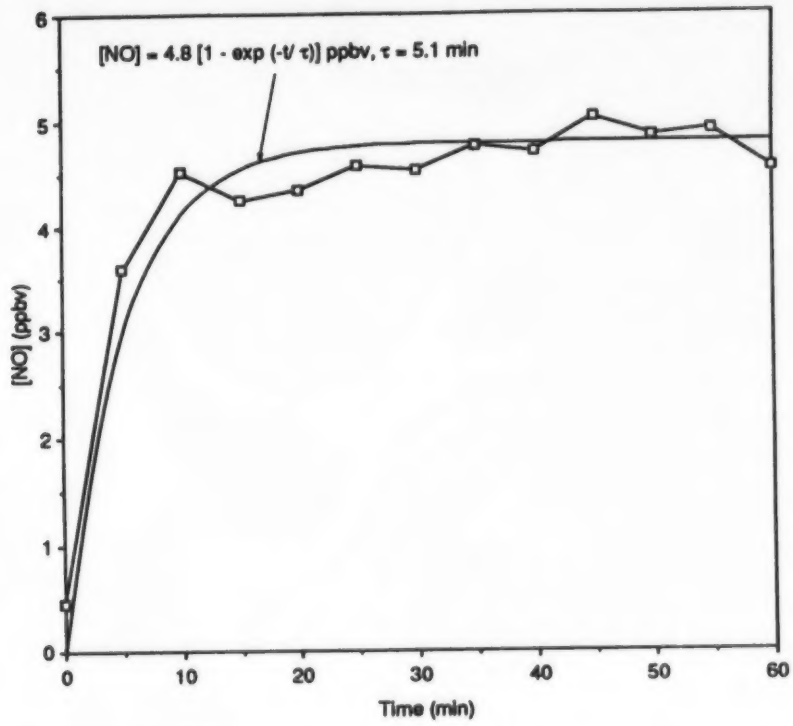

FIGURE 3

CHAMBER NO CONCENTRATION VERSUS TIME. SOIL NO FLUX MEASUREMENT AT EGBERT, SEPTEMBER 2, 1988, 1030 TO 1130 EDT. A THEORETICAL CURVE IS SHOWN FOR COMPARISON (SEE TEXT).

The soil emission values for each measurement period were calculated (see Appendix E for details) using the average NO values from 35-60 min (denoted $[NO]_{ss}$) as, in all cases, a stable steady state concentration appeared to have been reached. Theory (equation 1) predicts that the concentration would have been within 95% of the steady state value at a time equal to 3τ (three times the chamber exchange time - about 15 min). The NO flux ranged from 0.91 to 2.7 ng(N) $m^{-2}s^{-1}$ which is consistent with values reported in the literature (Mackay, 1988). These values may be in error by up to 10% due to uncertainties introduced by the baseline NO level in the scrubbed air (Appendix D and Appendix F).

TABLE 1

NO EMISSION FLUXES MEASURED AT EGBERT

Day	Time	Plot	Chamber Flow (L min^{-1})	$[NO]_{ss}$ (ppbv)	J (NO flux) (ng(N) $m^{-2}s^{-1}$)
Aug 29	1755-1820	1	5.5	1.56	0.91
Aug 30	1605-1630	1	5.5	2.03	1.2
Sept 2	1105-1130	1	5.3	4.80	2.7
Sept 2	1325-1350	1	5.2	3.27	1.8
Sept 2	1535-1600	2	5.2	3.47	1.9

4.0 SUGGESTED IMPROVEMENTS

The apparatus is basically ready to commence automated runs, but it is suggested that a reliable calibration procedure capable of generating flows containing NO_x at ppbv levels be established that can be used frequently (daily is preferred). A permeation tube system is suggested for NO_2 and flow dilution of a standard gas mixture for NO.

To facilitate ease of operation, a few minor adjustments could be made: lengthening the thermocouple wires (they are 50 ft long), replacing the skirts with thinner ones (1/8" steel is hard to drive into the ground), and replacing the metal frame with an aluminum one to reduce overall weight.

5.0 CONCLUDING REMARKS

A system for measuring the natural emission fluxes of NO_x from soils was constructed and field tested. Fluxes obtained on a grass and alfalfa field at Egbert during the Canadian Atmospheric Chemistry Study ranged from 0.91 to 2.7 ng(N) $m^{-2}s^{-1}$, consistent with values determined elsewhere for unfertilized fields.

It is recommended that future experimental work address the following questions:

- How representative of spatial and temporal averages are point measurements of NO_x emission fluxes?.
- Can NO_x emission rates be estimated on the basis of land use, soil type, season, etc., for modelling purposes?

Modelling should proceed in parallel to examine the relative importance of natural NO_x emissions to rural oxidant levels, and the degree to which these levels are perturbed by additional anthropogenic emissions.

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APPENDIX A

A.1 MATERIALS FOR NO_x EMISSION FLUX MEASUREMENT SYSTEM

A.1.1 Materials and Equipment

- polycarbonate chamber, 30 cm x 30 cm x 30 cm, Teflon-lined, with ceiling fan
- steel skirts (2), Teflon lined
- motor and frame to raise chamber
- air pump
- charcoal traps (2)
- desiccant (Drierite)
- UV lamp
- flow controllers (10 L/m, 10 mL/m) and control box
- LMA-3 NO_2 analyzer
- LNC-3 NO converter
- Teflon tubing
- IBM PC or compatible
- DAS-16-F data acquisition card
- Labtech Notebook data acquisition software
- Campbell Scientific 21X micrologger and optical isolator
- Vaisalla relative humidity probe and calibrator
- soil temperature probes
- electronic barometer
- Gill anemometer

A.1.2 Summary of Output/Input Voltage Ranges

	Voltage Output	Control Input
Motor	-	2.5 V
Luminox	0-2 V (up to 5)	-
Thermocouples	~0-2 MV	-
Vaisalla probe	0-100 mV	-
Electric barometer	0±100 mV	-
Solenoid	-	2.5 V

A.2 SUGGESTED TESTING PROTOCOL

1. Equipment Checks

Pre-assembly - test range and sensitivity of NO_x monitor, check calibration

- establish working order of pump, flow regulators, fan, sensors, motor

- check effectiveness of charcoal trap

Post-assembly - test gas adsorption by system

- measure internal air pressure change caused by chamber flow

2. Field Tests

- determine appropriate flow rate and equilibration time

- determine concentration vs time relationship for t = 0 to steady state
- establish precision

3. Field Studies

In field studies of NO_x emissions the following factors should be examined/monitored:

3.1 Temporal Variation

- diurnal variation

- 24-h surveillance over same plot, reading every 30 min

- 3 times for each plot, 3 plots per site

3.2 Spatial Variation

3.2.1 Local

- 10 different plots per site, similar soil and vegetation types

3.2.2 Regional

- compare data from several sites

3.3 Moisture Effects

- record amount and time of natural rainfall
- measure NO_x immediately following rain and as soil dries
- measure soil moisture periodically throughout study

3.4 Atmospheric and Soil Parameters

- measured concurrently with NO_x analysis
  - air temperature, RH
  - soil temperature (at various depths)
  - barometric pressure
- these should be measured inside and outside the chamber before commencing tests.

3.5 Ambient NO_x Levels

- study effect of increasing background NO_x on soil emission using known NO_x input concentrations from calibrator
- determine compensation point (where net flux approaches zero)

3.6 Soil Characteristics

- analyzed at beginning and end of session:
  - pH
  - organic content
  - bulk density
  - total N, as NH_4^+, NO_3^-, NO_2^-
- analyzed once:
  - soil texture
  - field capacity

3.7 Additional Information

- vegetation type and biomass
- field crop and fertilizer history
- soil type

A.3 DETAILS OF AUTOMATED SYSTEM

A personal-computer based system was developed to control the sampling system and to log data. The system was based around an IBM-PC XT compatible computer and a DAS-16-F board with Lab Tech Notebook software. To initiate the measurement process, the computer sent a 2.5 V signal to the motor which then lowered the chamber to ground level. After equilibrium NO_x levels were reached in the chamber, sampling commenced at a rate of 0.1 Hz and continued for 350 s, at which time the motor raised the chamber. During the sampling period the converter automatically switched between NO_2, NO_x and "zero" modes at 2 min intervals. The initial few data were discarded as the instrument was still settling down. Normally the LNC-3 outputs a status signal which identifies the mode in which the NO_x monitor is operating, as follows:

5 V ---> NO_x, total (NO + NO_2)
0.6 V ---> NO_2 only
2.5 V ---> zero

However, since the DAS-16-F board was calibrated to 0-2 V the status signals were:

2 V ---> NO_x
0.6 V ---> NO_2
2 V ---> zero

Since the instrument always cycled in the order shown confusion was avoided.

During the sampling time a separate, Campbell 21X micrologger collected data from the thermocouples, electronic barometer, and humidity probe and sent these every 5 min to Labtech Notebook via RS-232. Since this data was collected separately it was put into a separate file called "RS232.PRN." The NO_x data was put into "NO_x.PRN."

After 250 s of sampling the motor was activated, raising the chamber and terminating NO_x sampling. The two solenoid valves were then energized causing the scrubbed air to bypass the chamber and enter the LNC directly. The scrubbed air was sampled every 12.5 s for 6 min and the data (to be subtracted later from the NO_x data) were stored in the File "Clean.PRN".

The chamber stayed in the raised position for approximately 21 min (1250 s), after which the solenoids re-routed the scrubbed air back through the chamber which was again lowered to the ground, completing the cycle. This procedure is suitable for 24-h surveillance of NO_x flux from a single plot.

The data stored in the "NO_x.PRN" file contained:

- the time of sampling
- NO_2, NO, "zero air" concentrations (in Volts)
- converter status (indicates whether NO_2, NO or zero was being read)
- motor status (indicates position of chamber)

The "RS232.PRN" file contained:

- time of sampling
- 21X reference thermocouple reading
- thermocouples 1-3
- barometric pressure
- relative humidity
- chamber air temperature (via Vaisalla)

The "clean.PRN" file contained:

- time of sampling
- NO_2, NO, "zero"
- converter status
- valve status (to ensure that chamber was bypassed)

Because all of the data were stored in PRN files, they were readily accessed using "Analyze" from the main menu in Labtech Notebook. When "Analyze" was selected, Lotus 1-2-3 was automatically invoked and any PRN file was imported into a worksheet. Unfortunately some additional characters (relics of some programming code) were also imported but these could easily be erased using the Lotus "Range Erase" function.

These data files so created should not be confused with the setup files accessed using the "save/recall" command from "Files" in the main menu of Labtech Notebook. The setup files include:

- "Tutorl" to "Tutor 5", used in the tutorials of the manual
- "Real", which stores the setup conditions for an automated run
- "NO_x" which has setup conditions for a run not acquiring any RS232 data
- "RS232" does not acquire any NO_x data
- "Wires" which monitors the setup status of the motor, valves, converter and NO_x level.

The latter three setup conditions can be used to check the various components of the system before an actual data acquisition run (using "Real") is performed.

<u>Files stored in Labtech Notebook File "Real"</u>

Ch	1-8	RS232	
	9	Output to motor Use WF1.PRN	output ch 0
	10	Motor status	input ch 0
	11	Motor status (calculated)	
	12	Time	

13	Converter status	input ch 1
14	NO_x reading	input ch 2
15	Control output to valves WF2.PRN	output ch 1
16	Time	
17	Valve status	input ch 3
18	Scrubbed air NO_x value (calculated)	
19	Converter status (calculated)	

Labtech Notebook File "NO_x"

11 channels, same as above (File "Real") without the RS-232 channels

Labtech Notebook File "RS232"

8 channels, same as ch 1-8 on "Real" file

Labtech Notebook File "WIRES"

Ch 1	output to motor	output ch 0
Ch 2	output to valve	output ch 1
Ch 3	motor status	input ch 0
Ch 4	converter status	input ch 1
Ch 5	NO_x reading	input ch 2
Ch 6	valve status	input ch 3

A.4 DAS 16-F Set-up

1. Required DAS 16-F settings: address H330 (decimal 816)

   unipolar

   0-2 V, resolution = 0.488 mV

   DMA ---> 1

   8 differential analog input channels

2. Wiring used in setup file "Real" (for normal data acquisition run)

   - Analog output 0 ---> 2.5 V to motor

     1 ---> 2.5 V to solenoids

   Analog input 0 ---> signal from motor

   1*---> converter status

   2*---> NO_x reading in volts, must be corrected with a calibration curve

   3 ---> solenoid status

   4*---> NO_x reading for scrubbed air

Notes:

*Converter will always cycle in order. Note that the board is presently set at 0-2 V analog input, thus

2 V = NO_x
0.6 V = NO_2
2 V = zero

*Two sets of signal wires are attached to the LMA-3 output BNC, the first for analog input ch 2 and the other for analog input ch 4.

3. Timing

T = 0	motor lowers (2.5 V signal). Valves de-energized (0 V)
T = 900 s	start of data acquisition
T = 1250 s	data acquisition stops
	motor raises (0 V signal)
	valves energized (2.5 V)
	data acquisition on scrubbed air begins
T = 1610 s	data acquisition on scrubbed air stops
T = 2500 s	motor lowers (2.5 V)
	valves de-energized (0 V)

Therefore, as presently programmed, the box spends about 20.8 min on the ground and 20.8 min in the air.

A.5 Campbell 21X PROGRAM Settings

Table 1

			05	5 s table execution
Reference Temperature for Thermocouples	1		P17	
		1	1	
Thermocouple	2		P14	
		1	3	
		2	1	
		3	1	
		4	1	
		5	1	
		6	2	
		7	1	
		8	0	
Relative Humidity	3		P02	
		1	1	
		2	4	
		3	5	
		4	6	
		5	1	
		6	0	
Chamber Air Temperature	4		P02	
		1	1	
		4	7	
		5	0.5	
		6	-5.0	
Barometer	5		P02	
		1	1	
		2	4	
		3	4	
		4	5	
		5	0.67728	
	6		P92	If Time
		1	0	(outputs to final storage)
		2	5	
		3	10	
	7		P77	Real Time
		1	10	
	8		P71	Average
		1	7	
		2	1	

This program will output to final storage, 5 min averages of data taken every 5 s. Only data in final storage is transferred via RS-232 to Labtech Notebook.

Note that the time must be set (using *5) and baud rate set (using *4).

APPENDIX B

Pressure Effects

Tests were carried out to determine if the airflow through the chamber produced a pressure difference with respect to the outside atmosphere. A pressure gauge with a scale of 0 to 3 inches of water (divided in 10ths of an inch) was used, although the gauge was not calibrated. The chamber was placed on a vinyl groundsheet on top of a table and was taped along all edges to ensure an airtight seal. The chamber has four orifices; for the humidity probe, air-in tubing, air-out tubing, and an extra 1/4 inch fitting originally designed for connection to a permeation tube calibrator. The LNC-3 and LMA-3 draw a sampling air flow of 1.5 L min^{-1} from the vent flow. The air flow was set at 5.5 and 10 L/min. The humidity probe was replaced by the pressure gauge and the remaining apparatus was set up as in a normal data acquisition run. The results were:

Condition	Pressure (in. of water)	Flow (L/min)
vent & fitting open	0.01	5.5
vent & fitting closed	0.27	5.5
vent closed, fitting open	0.03	5.5
vent closed, fitting open	0.1	10
vent closed, fitting closed	0.6	10

0.1 inch of water is approximately 0.25 mbars. For the remaining runs, the vent and the fitting were left open and the flow set to ~5.5 L/min.

APPENDIX C

Instrumentation Effects

To determine the effects of passage of the air sample through the apparatus on measured concentrations of NO and NO_2, ambient air containing NO_x at low levels (ppbv or less) was passed through various combinations of the scrubber system, the LNC-3 and the LMA-3. Initially, inconsistent results were obtained at indicated NO and NO_2 levels of about 1 ppbv. When the teflon-tubing in the system was replaced, results became more consistent with indicated NO_2 levels in the scrubbed air flow of 0.01 ppbv and NO levels of 0.1 to 0.5 ppbv. These results show that care should be taken to use uncontaminated teflon-tubing in all lines and suggest that hold-up and slow release of some NO_x occurs within the LNC-3.

APPENDIX D

MEASUREMENTS OF NO_x EMISSIONS FROM SOILS AT EGBERT

TABLE D1

CHAMBER DATA, Plot 1, August 29, 1988

Start: 1720
Ambient RH: 42%
Ambient Temp: 28°C

Time (min)	Chamber Air Temp (°C)	Chamber Air RH (%)	NO_2 ppbv	NO ppbv
5	26.5	48	-	-
10	25.0	64	0.05	1.35
15	24.0	68	0.04	1.35
20	22.8	72	0.03	1.32
25	22.0	75	0.03	1.23
30	21.2	78	0.02	1.23
35	20.8	79	0.01	1.16
40	20.2	81	0.01	1.12
45	20.0	82	0.01	1.10
50	19.8	83	0.01	1.08
55	19.7	84	0.01	1.07
60	19.5	84	0.01	1.06

End: 1820	NO_2 (ppbv)	NO (ppbv)
Ambient Air:	0.93	0.77
Scrubbed Air:	0.01	0.12

Ambient Temp: 18°C
Ambient RH: 66%
Flow: ~5.5 L/min

NOTE: All NO and NO_2 concentrations given are uncorrected instrument readings.

TABLE D2

CHAMBER DATA, Plot 1, August 30, 1988

Start: 1530
Ambient RH: 47%
Ambient Temp: 23°C

Time (min)	Chamber Air NO_2 (ppbv)	Chamber Air NO (ppbv)
5	0.05	0.81
10	0.05	0.92
15	0.07	1.16
20	0.07	1.34
25	0.07	1.31
30	0.13	1.41
35	0.08	1.60
40	0.13	1.60
45	1.12	1.66
50	0.06	1.58
55	0.06	1.51
60	0.06	1.45

End: 1630	NO_2 (ppbv)	NO (ppbv)
Ambient Air:	0.478	0.542
Scrubbed Air:	0.04	0.24

Flow ~5.5 L/min

NOTE: All NO and NO_2 concentrations given are uncorrected instrument readings.

TABLE D3

CHAMBER DATA, Plot 1, Trial 1, September 2, 1988

Start: 1030 NO_2(ppbv) NO(ppbv)
Ambient Air: 6.89 3.08
Scrubbed Air: 0.033 0.333

Time	Chamber Air			Scrubbed Air		
(min)	RH (%)	NO_2 (ppbv)	NO (ppbv)	NO_2 (ppbv)	NO (ppbv)	
5	-	0.12	3.14	0.02	0.30	
10	-	0.10	4.07	0.02	0.29	(est)
15	-	0.09	3.80	0.02	0.28	
20	61	0.09	3.89	0.02	0.27	
25	60	0.07	4.12	0.02	0.27	
30	58	0.04	4.08	0.02	0.29	
35	58	0.09	4.30	0.02	0.29	
40	57	0.08	4.25	0.02	0.29	
45	56	0.09	4.57	0.02	0.28	
50	55	0.10	4.40	0.02	0.31	
55	56	0.08	4.45	0.02	0.25	
60	56	0.14	4.09	0.01	0.26	

End: 1130 NO_2 (ppbv) NO (ppbv)
Ambient Air: 2.28 1.41
Box Temp: 32°C
Air Temp: 26°C
Air RH: 40-50%
Flow: ~5.25 L/min

NOTE: All NO and NO_2 concentrations given are uncorrected instrument readings.

TABLE D4

CHAMBER DATA, Plot 1, Trial 2, September 2, 1988

Start: 1250	NO_2(ppbv)	NO(ppbv)
Ambient Air:	1.43	3.77
Scrubbed Air:	0.02	0.32
Ambient RH:	26%	

Time	Chamber Air			Scrubbed Air	
	RH	NO_2	NO	NO_2	NO
(min)	(%)	(ppbv)	(ppbv)	(ppbv)	(ppbv)
5	35	0.13	1.76	-	-
10	-	0.15	2.22	0.03	0.27
15	43	0.15	2.52	-	-
20	46	0.15	2.49	0.03	0.25
25	47	0.11	2.77	-	-
30	-	0.12	2.62	0.02	0.22
35	50	0.11	2.75	-	-
40	49	0.08	2.72	0.02	0.19
45	52	0.06	2.92	-	-
50	52	0.06	2.77	0.03	0.20
55	54	0.06	3.01	-	-
60	52	0.10	2.68	0.02	0.20

End: 1350	NO_2(ppbv)	NO(ppbv)
Ambient Air:	1.36	0.84
Ambient RH:	45-50%	
Flow:	~5.16 L/min	

NOTE: All NO and NO_2 concentrations given are uncorrected instrument readings.

TABLE D5

CHAMBER DATA, Plot 2, September 2, 1988, Plot 2

Start: 1500 NO_2(ppbv) NO(ppbv)
Ambient Air: 1.19 0.52
Scrubbed Air: 0.03 0.21
Ambient RH: 22-30%

Time	Chamber Air			Scrubbed Air	
	RH	NO_2	NO	NO_2	NO
(min)	(%)	(ppbv)	(ppbv)	(ppbv)	(ppbv)
5	-	0.09	1.86	-	-
10	54	0.06	2.58	0.01	0.13
15	54	0.06	3.07	-	-
20	53	0.06	2.95	0.02	0.12
25	56	0.06	3.12	-	-
30	54	0.05	2.89	0.02	0.10
35	56	0.04	3.02	-	-
40	55	0.05	2.89	0.02	0.12
45	55	0.06	3.03	-	-
50	54	0.05	2.94	0.02	0.11
55	56	0.05	3.13	-	-
60	53	0.04	3.07	0.02	0.11

End: 1600 NO_2(ppbv) NO(ppbv)
Ambient Air: 2.50 1.97
Ambient RH: 35-40%
Flow: ~5.17 L/min

NOTE: All NO and NO_2 concentrations given are uncorrected instrument readings.

APPENDIX E

Method of Calculation of NO Emission Flux from Data of Appendix D

Attainment of Equilibrium

$T_{equil} = 3VQ^{-1}$ (95% steady state)
$V = 31.5$ L (box dimensions: 0.3x0.3x0.3 m, sat ~5 cm above soil surface on skirt)

At $Q = 5.1$ L/min NTP
$T_{equil} = 18.5$ min

V = chamber volume
Q = flow

Steady state concentration (ΔN_{ss})
$\Delta N_{ss} = [NO]_{out} - [NO]_{in}$ at steady state
$\Delta N_{ss} = JAQ^{-1}$, therefore
$J = \Delta N_{ss} QA^{-1}$

J = NO flux
A = plot area

Units: J ---> ng (N)m^{-2} s^{-1}
A---> m^2
ΔN_{ss}---> ng (N) L^{-1}
Q---> L s^{-1}

Conversion ---> 1 ng (N) L^{-1} = 1.6 ppb
Since 1 mole NO or NO_2 ---> 22.4 L (STP), 24.21 L (1 atm, 20°C)
14 g (N) ---> 22.4 L (STP)
0.625 g (N) ---> 1 L
therefore 1 ng (N) L^{-1} = 1.6 ppb (STP), 1.7 ppbv (1 atm, 20°C)

APPENDIX F

PROPERTIES OF THE EGBERT SOIL

Organic Matter	2.5%
pH	7.1
Texture: Fine Sandy Loam	
Clay	7.2%
Silt	27.6%
Sand	65.2%

Phosphorus	9 mg/kg
Potassium	38 mg/kg
Magnesium	92 mg/kg
Calcium	1436 mg/kg

APPENDIX G

CALIBRATION OF NO, MONITOR

The Luminox LMA-3 monitor was calibrated in the field using a permeation tube calibration system belonging to Atmospheric Environment Service (AES). The four-point calibration is shown in figure G1. The instrument response is linear in the region between 1.5 and 3.5 ppbv of NO_2 (1 to 3 ppbv indicated reading). Below 1.5 ppbv (1 ppbv indicated) the response becomes non-linear. All steady-state NO concentrations in the field experiment were in the range of linear response. Unfortunately, the inlet concentrations ("scrubbed" air) were in the sub-ppbv range (typically 0.1 to 0.3 ppbv indicated). The calibration range did not extend to this region, however, extrapolation of the calibration curve suggests that these values may have been simply due to instrument offset. It was therefore assumed that the inlet concentration, N_{in}, was zero in order to calculate emission fluxes. It was estimated that the potential error in the flux so induced was less than +10%. The LNC-3 was also assumed, for lack of data at low concentration, to have a NO to NO_2 conversion efficiency of 92% as specified by the manufacturer.

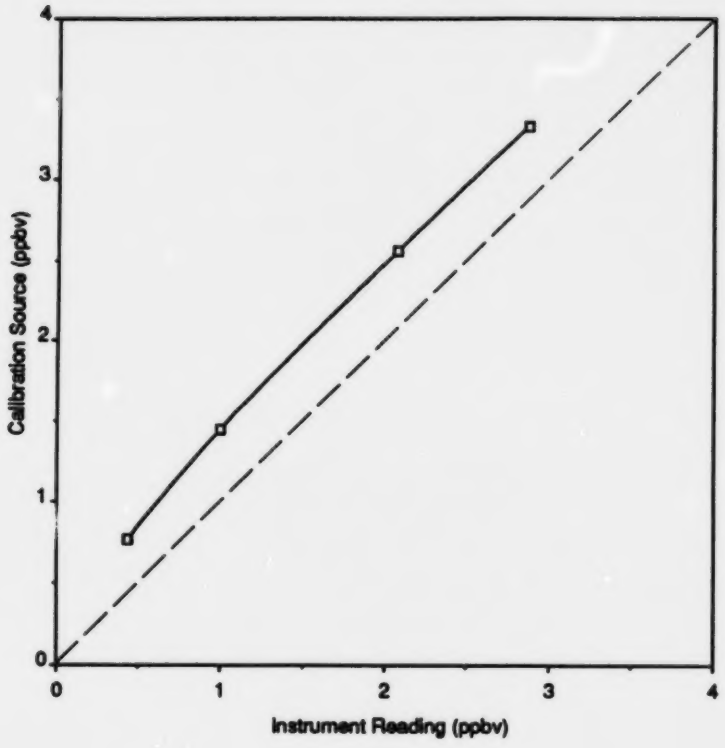

FIGURE G1

FOUR-POINT NO_2 CALIBRATION CURVE FOR NO_X ANALYZER USED IN FIELD NO_X EMISSION RATE MEASUREMENTS